SCIENCE FOR CERAMIC PRODUCTION

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REFRACTORY CERAMICS BASED ON LOCAL MATERIALS

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A technology for producing ShA and ShB refractories uses high-melting clays from the Rostov Region and high-alumina technogenic waste. The effect of the chamotte-to-clay ratio, the granulometric composition, and the additive introduction method on the properties of products is investigated.

In view of the absence of natural mineral deposits for refractory products in the Rostov Region, it appears important to develop technologies for producing refractories from local materials. The main material sources used in our study were high-melting clay of grade 1 from the Vladimirovskii deposit containing up to 30% Al_2O_3 and high-alumina waste from the Belokalitvinskii Metallurgical Works. The possibility of using them to make refractory products ShA and ShB (GOST 390–96) has been investigated.

Clay VK-1 has the following chemical composition (here and elsewhere, wt.%): 54.60 SiO_2, 29.80 Al_2O_3, 2.10 Fe_2O_3, 1.00 TiO_2, 1.20 CaO, 1.00 MgO, 3.40 ($K_2O + Na_2O$), 9.75 calcination loss, 16.60 free quartz. The mineralogical composition of this clay is represented by the following crystalline phases (%): 33 – 48 kaolinite, 20 – 23 hydromica, 8 – 14 montmorillonite, 10 – 20 quartz, 2 – 3 feldspar, and 2 impurities.

Technological Properties of Clay

Calcination loss, %	9.75
Residue on No. 063 sieve, %	4.5
Content of particles of size below 0.001 mm, %	65.6
Plasticity number, %	19.2
Sintering temperature, °C	1100 – 1150
Sintering interval, °C	100 – 150
Water absorption of sintered clay, %	< 2
Melting temperature, °C	1600 – 1720

Based on the published and factory data, the clay – chamotte ratio was taken equal to 60 : 40 and 40 : 60. The chemical composition of mixtures for ShB-grade, class B products are listed in Table 1.

It can be seen in the calculation data that the amount of Al_2O_3 in mixtures 1 and 2 satisfies the requirements of GOST 390–96 for the production of ShB brick and is equal to 30.1 and 30.7%, respectively [1].

To obtain ShA brick, instead of technical alumina, 3 – 5% alumina-bearing waste was introduced into the ceramic mixture. The chemical composition of the alumina-bearing waste (AW) is (%): 14.53 SiO_2, 69.27 Al_2O_3, 1.87 Fe_2O_3, 1.70 CaO, 5.32 MgO, 0.31 TiO_2, 3.32 PzO_5, 0.05 MnO_2, and 3.03 K_2O.

The chemical compositions of mixtures for ShA articles are listed in Table 2. It can be seen that all mixtures satisfy the requirements on Al_2O_3 content (at least 33%).

The properties of chamotte (the degree of sintering and granular composition) have a significant effect on the quality of chamotte products. Therefore, special attention is focused on producing high-quality chamotte.

In developing the clay firing procedure to obtain chamotte, we were guided by data determining the modification of the physical and mechanical properties of products in firing [2]. The clay from the Vladimirovskii deposit is a high-melting plastic material. To determine the sintering temperature, experiments were performed within a temperature interval of 1200 – 1300°C with a step of 50°C. The water absorption of clay VK-1 after firing at 1200°C was equal to 7.2%, 4.7% at 1250°C and less than 2.0% at 1300°C.

The thermographic analysis indicated that the dehydration of argillaceous materials proceeds at a high rate within a

TABLE 1

Mixture	Material	Weight content, %							
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	calcination loss
1	Clay, 60%	31.7	17.3	1.2	0.6	0.7	0.6	2.0	5.7
	Chamotte, 40%	23.5	12.8	0.9	0.4	0.5	0.4	1.5	–
2	Clay, 40%	21.2	11.6	0.8	0.4	0.5	0.4	1.3	3.8
	Chamotte, 60%	35.2	19.1	1.3	0.7	0.8	0.7	2.2	–

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TABLE 2

Mixture	Material	Weight content, %							
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	calcination loss
3.1	Clay, 58.2%	30.9	16.8	1.2	0.6	0.7	0.6	1.9	5.5
	Chamotte, 38.8%	23.7	12.3	0.9	0.4	0.4	0.4	1.4	–
	AW, 3.0%	0.4	2.1	0.1	–	0.1	0.2	0.1	–
	Ceramic mixture	55.0	31.2	2.2	1.0	1.2	1.2	3.4	5.5
	Ceramic	58.0	33.0	2.3	1.1	1.3	1.3	3.6	–
3.2	Clay, 38.8%	20.6	11.2	0.8	0.4	0.5	0.4	1.2	3.7
	Chamotte, 58.2%	34.2	18.6	1.2	0.6	0.8	0.6	2.2	–
	AW, 3.0%	0.4	2.1	0.1	–	0.1	0.2	0.1	–
	Ceramic mixture	55.2	31.9	2.1	1.0	1.4	1.2	2.5	3.7
	Ceramic	57.3	33.1	2.2	1.0	1.5	1.2	2.6	–
4.1	Clay, 57.1%	30.3	16.5	1.1	0.6	0.7	0.6	1.9	5.4
	Chamotte, 37.9%	22.3	12.1	0.8	0.4	0.5	0.4	1.4	–
	AW, 5.0%	0.7	3.6	0.1	–	0.1	0.3	0.2	–
	Ceramic mixture	53.3	32.1	2.0	1.1	2.3	1.3	2.5	5.4
	Ceramic	56.3	33.9	2.1	1.2	2.4	1.4	2.6	–
4.2	Clay, 37.9%	20.1	10.9	0.8	0.4	0.5	0.4	1.3	3.6
	Chamotte, 57.1%	33.6	18.3	1.1	0.6	0.7	0.6	2.2	–
	AW, 5.0%	0.7	3.6	0.1	–	0.1	0.3	0.2	–
	Ceramic mixture	54.4	32.8	2.0	1.0	1.3	1.3	2.7	3.6
	Ceramic	56.4	34.0	2.1	1.0	1.3	1.3	2.8	–

temperature interval of 300 – 800°C. The major part of shrinkage is observed in the temperature interval of 900 – 1200°C in the range of the first and second exothermic effects. The rate of the temperature rise and an exposure longer than 1 h have an insignificant effect on the process; therefore, the temperature of firing clay to be used as chamotte chosen as the optimum was 1250°C with an exposure of 1 h. This treatment schedule provides for chamotte with water absorption below 5%.

Ceramic mixtures for producing chamotte consist of clay mixed with chamotte and water. A correct choice of the granulometric composition of the materials, primarily chamotte, is significant for obtaining a dense preform. Theoretically the grain should have sharp facets. With such a shape the grain has a larger active surface. The practice of chamotte production involves grinding usually performed in ball mills yielding rounded grains. A correct choice of the fractional composition of such grains provides for the densest packing [3, 4].

Two chamotte compositions for mixtures ShA and ShB were investigated. The fineness of clay milling was below 3 mm. The granulometric composition of chamotte is indicated in Table 3. Samples were prepared by plastic and semidry molding with mixture moisture equal to 20% (variants 1 and 3) or 10% (variants 2 and 4). The molding pressure was 20 MPa and the firing temperature was 1300°C. The properties of chamotte refractories are presented in Table 4.

The analysis of the results obtained indicates that the optimum method for producing ShB refractories is semidry molding with the granulometric chamotte composition corresponding to composition 1.

TABLE 3

Chamotte composition	Quantity of fractions, %, of size, mm		
	3 – 2	2 – 0.5	< 0.5
1	25	15	60
2	10	30	60

TABLE 4

Mixture	Chamotte composition	Water absorption, %		Compressive strength, MPa		Additional shrinkage, %
		semidry molding	plastic molding	semidry molding	plastic molding	
		Refractories ShB				
1	1	10.4	13.0	26.7	26.0	0.8
1	2	7.4	8.0	17.0	17.0	0.9
2	1	2.6	6.6	36.1	26.7	0.6
2	2	5.4	7.0	36.1	26.7	0.5
		Refractories ShA with AW added into mixture				
3	1	13.0	17.0	16.0	19.0	0.9
3	2	10.0	12.0	20.0	16.0	1.1
4	1	4.1	6.5	25.6	24.2	0.5
4	2	3.6	4.0	25.0	26.7	0.7
		Refractories ShA with AW added into chamotte				
3	1	6.7	7.0	25.4	30.5	0.9
3	2	5.8	5.6	24.0	23.0	1.1
4	1	7.0	9.5	25.6	24.5	0.7
4	2	9.5	12.9	21.9	24.9	0.7

For introducing AW into mixtures, the composition of 40% clay and 60% chamotte is optimal for both semidry and plastic molding. The granulometric composition of chamotte

in such mixtures has no significant effect on the properties of the product.

The best results for ShA compositions were obtained when AW was added directly to the mixture for semidry molding. [4]. Additional shrinkage of the optimum compositions is less than 0.7%, the compressive strength is over 15 MPa, and the thermal strength is 10 – 15 thermal cycles.

The resulting ShB and ShA articles meet the requirements of GOST 390–96 imposed on chamotte refractories.

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